PIGMENTS, ORGANIC

1. Introduction

Pigments are colored, fluorescent, or pearlescent particulate organic or inorganic finely divided solids that are usually insoluble in, and essentially physically and chemically unaffected by, the vehicle or medium in which they are incorporated. They alter appearance either by selective absorption, interference and/or scattering of light. They are usually incorporated by dispersion in a variety of systems and retain their crystal or particulate nature throughout the pigmentation process (1). The large number of systems vary widely from paints to plastics to inks and fibers.

Dyes, on the other hand, are colored substances that are soluble or go into solution during the application process and impart color by selective absorption of light. In contrast to dyes, whose coloristic properties are almost exclusively defined by their chemical structure, the properties of pigments also depend on the physical characteristics of its particles.

In some cases, a single chemical substance can serve both as a dye and as a pigment. For example, indanthrone [81-77-6] (Pigment Blue 60) functions as a blue pigment or as a dye. As a pigment, indanthrone is a particulate, insoluble solid dispersed directly into a vehicle, whereas as a dye it is reduced to a base-soluble hydroquinone derivative and then reoxidized onto a solid substrate.

The description of colored organic pigments excludes consideration of inorganic pigments, as well as most black pigments that consist of specially treated forms of carbon and white pigments that are entirely of inorganic origin (see PIGMENTS, INORGANIC). Organic pigments are generally stronger and brighter than their inorganic counterparts and range in color over the entire visible spectrum. However, because of the structure complexity of organic pigments and the method of their manufacture, they are invariably higher in cost. Many organic pigments do not possess the stabilities shown by some inorganic counterparts, nevertheless some organic pigments are sufficiently durable and stable to fit most modern and potential applications. In fact, many inorganic pigments that contain heavy metals such as chromium and cadmium are being replaced by carefully chosen organic substitutes.

Some commercially significant organic pigments are listed in Table 1.

Pigments are categorized according to their generic name and chemical constitution in the *Colour Index* (CI), published by the Society of Dyers and Colourists (2). For example, copper phthalocyanine is designated CI Pigment Blue 15, CI number 74160 and is further identified by the Chemical Abstract (CAS) Registry Number [147-14-8]. In practical terms, manufacturers have their own name for a particular pigment, with variations depending on the applications for which it is designed. In this article, pigment structures are identified by their abbreviated pigment designations, eg, PB 60, for the convenience of the reader in associating the color hue with the structure. The abbreviations PY, PO, PR, PV, PB, and PG, designate yellow, orange, red, violet, blue and green pigments, respectively.

Pigments are available in a number of commercial forms including dry powders (either surface treated or untreated), presscakes, flushed colors (thick pastes), fluidized dispersions (pourable pastes), resin predispersed pigments (powders), and plastic color concentrates or master batches (granules) (see PIGMENT DISPERSIONS).

Significant pigment attributes are tinctorial strength, durability (photochemical stability), hiding power, transparency, and heat and solvent resistance. Other properties include brightness (saturation), dispersibility, gloss, rheology, crystal stability, bleed resistance, flocculation resistance, and other properties associated with specialized applications.

The history of synthetic organic pigment discovery began in the middle of the nineteenth century. In 1856, William H. Perkins at the age of 18 synthesized for the first time the color mauveine [6373-22-4] by oxidizing aniline containing toluidine with chromic acid. This event ushered in an era of colored synthetic chemistry that continues into the 2000s. Many new organic structures have been discovered and introduced as commercial organic pigments.

The initial synthetic developments were concerned primarily with dyestuffs for the textile industry, and the period up to 1900 was characterized by the discovery and development of many dyes derived from coal-tar intermediates. Rapid advances in color chemistry were initiated after the discovery of diazo compounds and azo derivatives (shown to be largely hydrazone derivatives). The wide color potential of this class of pigments and their relative ease of preparation led to the development of azo colors, which represent the largest and most diverse fraction of manufactured organic pigments. Commercial development began with the discovery of Lithol Red in 1899. After World War I among the most important pigments produced in the United States were Toluidine Red [2425-85-6], Lake Red C [5160-02-1], and Hansa Yellow [2512-29-0]. Azo condensation pigments were discovered in 1951. At present, of all worldwide manufactured synthetic organic pigments, 59% by volume belong to the azo family which is estimated to be part of an $\sim$ \$5.2 billion worldwide organic pigment market expected to increase to \$5.5 billion in 2004 and about \$7.5 billion in 2009 (3) (see AZO DYES).

The development in 1913 of the brilliant lakes of complex heteropoly acids of phosphorus, molybdenum, and tungsten with basic dyes like Rhodamine B [81-88-9], Victoria Blue [56646-84-5], or Methyl Violet [8004-87-3], led to development of superior fastness pigments relative to the tannin tartar emetic precipitations of the same dyes. Still these pigments were not sufficiently durable for outdoor use. The largest single advance in pigment technology after World War I was the discovery of the relatively complex structure, but easily synthesized copper phthalocyanines, which were characterized by excellent brightness, strength, bleed resistance, and lightfastness. Copper phthalocyanines share of the world market stands at 29% by volume (4) (see PHTHALOCYANINE COMPOUNDS).

After World War II the most important discovery was the family of red-violet quinacridone pigments, followed by the mostly yellow-orange benzimidazolones and isoindolinone pigments, and the most recent development of the red-orange diaryl pyrrolopyrroles. These pigments belong to a group referred to as high performance pigments (HPPs). These and other polycyclic pigments belonging to this important group are defined as pigments that demonstrate unique and superior properties for their intended use. The volume of organic HPPs (Historically the copper phthalocyanines have been excluded from the HPP group and combined with the classical or commodity pigments, notwithstanding their excellent pigmentary properties.) sold worldwide totals in excess of 20,000 tons, with sales approaching \$1.5 billion (5).

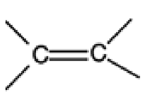
Finding a totally new pigment class or chromophore is a rare event. The latest commercialization of a new family of pigments is represented by the pyrrolopyrroles discovered in 1983. The discovery years of important pigments are compiled in the table below.

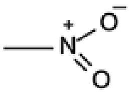
Pigment name	Year	Pigment name	Year
Perkin's Mauve	1856	Copper Phthalocyanine Blue	1935
Lithol Red	1899	Copper Phthalocyanine Green	1938
Indanthrone Blue	1901	Perylenes	1950
Toluidine Red	1905	Carbazole Violet	1952
Hansa Yellow	1909	Azo condensation pigments	1951
Diarylide Yellow	1911	Quinacridones	1955
Heteropolyacid complexes with basic dyes	1913	Benzimidazolones	1960
Red 2B	1931	Diaryl pyrrolopyrroles	1983

In the discovery of colored pigments, the basic synthesis of the pigment is only the beginning of an important development effort. A significant challenge comes in reducing and/or controlling particle size, particle shape, particle size distribution, and conditioning of pigments to achieve desired dispersibility, flocculation resistance, rheology, and other working properties. A large and creative effort goes into the modification of pigments to improve their chemical, photochemical, and physical properties.

2. Color and Constitution

As early as 1868 Graebe and Liebermann (6) recognized that color in organic compounds is associated with the presence of multiple bonds. A few years later Witt (7) coined the term chromophore, from the Greek *chroma* meaning color and *phoros* meaning bearer, for groups that give rise to color. The term is used to designate π-electron-containing moieties (conjugated double bonds), which contribute to the selective absorption of visible light. Generally, organic compounds absorb light in the ultraviolet (uv) (210–400-nm) and visible (vis) (400–750-nm) region of the spectrum at characteristic wavelengths. The intensities of these absorptions vary due to the excitation of the more loosely held electrons in the molecule. All unsaturated groups have remarkably similar π–π^* transitions regardless of the atoms contained in the common chromophores.


ethenyl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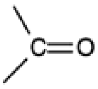
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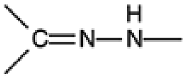
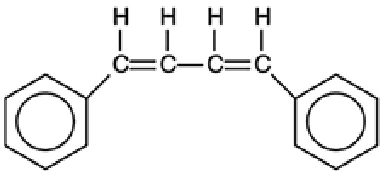

hydrazone

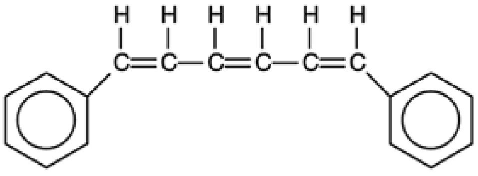
Isolated, unconjugated chromophoric groups absorb at $\sim$ 200 nm, at the end of the uv spectrum. Ethylene absorbs at 162.5 nm. Conjugation shifts absorption to longer wavelengths. Butadiene absorbs at 217 nm, and benzene shows its primary absorption at 254 nm. The π electrons in conjugated hydrocarbons tend to be more readily separated from their nuclei, leading to excited states that are more polar than the ground states.

Incorporation of substituents into aromatic systems that are electron donating, eg, hydroxy, methoxy, amino, alkylamino, and dialkylamino, tend to shift light absorption to longer wavelengths (bathochromic shifts). Such groups are known as auxochromes, from the Greek *auxo* meaning increase. They are auxiliaries to the chromophores and enhance and modify absorption and color by virtue of their nonbonding electrons. Groups that withdraw electrons have the opposite effect, making electron excitation less facile, and consequently shift absorption to shorter wavelengths (hypsochromic shifts).

The presence of π–π or n–π conjugated systems does not ensure absorption of visible light or generation of color. However, all colored organic compounds, including pigments, possess extended conjugated resonance systems. Thus, whereas 1,4-diphenylbutadiene is colorless, 1,6-diphenylhexatriene is colored.

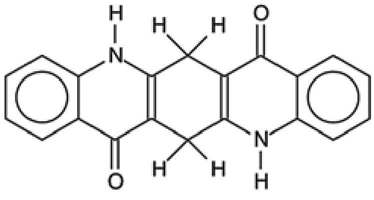


colorless

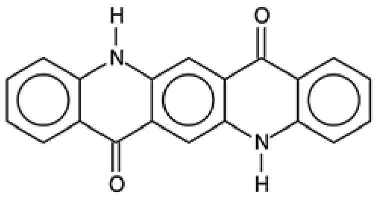


colored

Similarly, 6,13-dihydroquinacridone is virtually colorless, whereas quinacridone is a colored pigment. Generally, the longer the conjugated system the longer the wavelength of the absorbed visible light.



colorless



colored

All absorbed light is complementary to reflected light that produces observed color. All colors are a function of the wavelength of absorbed light as shown in Table 2 (see COLOR). Thus, if a pigment absorbs only blue light it imparts an orange color, whereas when it absorbs orange light the observed color is blue.

3. Properties

The physical and chemical characteristics that control and define the performance of a commercial pigment in a vehicle system include its chemical composition, chemical and physical stability, solubility, particle size, shape and particle size distribution, degree of dispersion, crystal morphology including polymorphic forms, refractive index, specific gravity, electronic spectra with particular emphasis on molar extinction coefficients in the visible spectrum, surface area, and the presence of impurities, extenders, and surface modifying agents. Invariably, a pigment is used in a vehicle system, therefore its ultimate performance in use derives from both physical and chemical pigment—vehicle interaction. Performance of most pigments is system dependent.

Unlike inorganic pigments, organic pigments are relatively strong and bright (saturated), but their fastness properties, though adequate for the purposes for which they are used, vary widely from poor to outstanding.

3.1. Strength. The inherent strength of a pigment depends on its light-absorbing characteristics that are related to its molecular and crystalline structure. In addition, strength is a function of particle size or surface area. The ability of a pigment to absorb light increases with decreasing particle size or increasing surface area, until the particles become entirely translucent or transparent to incident light. Particle size reduction beyond this point does not increase tinctorial strength of a pigmented system. Specific surface areas of organic pigments are typically in the range of 10–100 m^2/g. Whereas most azo pigments are prepared in pigmentary form by aqueous precipitation processes, most other pigments are synthesized in nonpigmentary crude form of relatively large crystal size up to 100 μm and subsequently reduced to pigmentary size of 0.01–0.5 μm either by attrition or precipitation processes. Being finely divided the particles have a great tendency to aggregate and agglomerate into crystal assemblies. To obtain the inherent strength of a pigment the aggregates must be completely broken down to individual crystals by application of work and their reagglomeration or flocculation prevented. Total breakdown to single crystals in practical systems seldom happens.

Pigment strength in a vehicle also depends on the typical character of other components in a pigmented system insofar as they absorb or scatter light. Strength comparisons are usually made with a series of samples featuring varying amounts of a pigment incorporated in a vehicle with a corresponding series in the same vehicle containing a reference pigment. Instrumental comparisons are commonly practiced.

A good absolute theoretical comparison of strength is represented by the area under the absorption bands in the visible spectrum, or less accurately by the molar extinction coefficients at the maximum wavelength of absorption. On that basis diarylide pigments are about three times stronger than most ordinary monoazo pigments, and copper phthalocyanines are also very strong pigments. With most pigments color strength does not increase continuously until the pigment is molecularly dispersed (8), i.e., it is in solution. Color strength passes through a maximum within the particle size range of 0.1–0.01 μm. This sets a limit to the potential color strength of a pigment dispersion.

3.2. Brightness or Saturation. The saturation of a colored pigment is a measure of its brightness or cleanliness as opposed to dullness of hue. Generally, if a pigment absorbs light over a wide range of wavelengths, ie, shows broad absorption bands, or contains more than one chromophore, the pigment is likely to be duller than a pigment with sharp absorption bands due to a single chromophore. Because pigments are frequently used in combinations or blends, the brightness is determined by the selective absorption of the individual pigments and this significantly affects the brightness of the reflected color. A saturated pigment provides flexibility in color blending and its use provides important economic advantages since desaturation can be accomplished by blending with duller and less expensive pigments, like carbon black [1333-86-4] or iron oxide [1309-37-1].

3.3. Fastness. The fastness of a colored pigment defines its inherent ability to withstand the chemical and physical influences to which it is exposed during and subsequent to its incorporation into a pigmented system. Fastness describes the characteristics of a pigment in terms of its color stability in a pigmented system upon exposure to light, weather, heat, solvents, or various chemical agents. Ideally, a pigment should be insoluble and chemically and photochemically inert. Only a few organic pigments approach such perfection. Fastness properties that are of practical significance are those observed for pigments incorporated into a coating or resin system under the exact conditions of incorporation and use.

The development of new resins, plastics, fibers, elastomers, etc, which are processed at progressively higher operating and curing temperatures has created a need for pigments that stand up for relatively long periods of time to a hostile environment. They must remain essentially unaltered when incorporated into plastics such as polypropylene, acetonitrile–butadiene–styrene (ABS), or nylon at relatively high temperatures. In reality, in high temperature plastics most organic pigments partially dissolve and undergo particle ripening or growth thus changing color without chemical destruction. Some pigments can change to thermodynamically more stable polymorphic forms with consequent color change, and others simply decompose.

Bleeding properties are also a function of solubility of a pigment in a vehicle, plasticizer, or solvent. Blooming is another manifestation of solubility whereby dissolved pigment migrates from within a pigmented medium to its surface where it is redeposited as pigment crystals and can be readily rubbed off. This is quite prevalent in the coatings (qv) and printing industries.

Once a pigment is incorporated into a system, it is expected to be durable and withstand the combined chemical and physical stresses of weather, solar radiation, heat, water, and industrial pollutants. Because a pigment is totally enveloped by the medium which is itself not inert, various pigments perform differently in different systems. Thus, a pigment may be lightfast or weatherfast in one system and fail in another. In addition, lightfastness or weatherfastness of an organic pigment is dependent on its particle size, since absorbed radiation by pigment particles largely determines the response of a system to light. Relatively little is known about the chemistry responsible for the destruction of organic pigments by solar radiation. However, since destructive light penetrates the pigment surface, the larger the surface area the faster the deterioration. Within a particle, light destroys one layer of molecules after another. Interior pigment molecules are preserved until outer layers are destroyed, therefore relatively large or thick particles resist light longer and are more durable. Thus, some pigments with high surface areas are usable only for indoor applications, and the same pigments with reduced surface areas (larger particle sizes), have found outdoor applications.

The quantitative measurement of pigment or pigmented system deterioration upon exposure to heat or light used to be expressed by visual numerical standards. In modern times color differences are expressed in the CIELAB system that has become the leading method for color characterization (9).

3.4. Dispersibility. The dispersibility of a pigment is measured by the effort required to develop the full tinctorial potential of a pigment in a vehicle system. Dispersibility differs from system to system depending on pigment–medium interaction and compatibility.

Small particle size pigments, especially the very small crystals, seldom exist as individual entities, but as strongly coherent aggregates or less firmly bound agglomerates. These are best examined by electron microscopy. Aggregation and agglomeration take place during organic pigment manufacture especially when individual crystals are being produced during attrition or precipitation processes. Aggregate formation is particularly pronounced during drying when water removal from capillaries between crystals causes crystals to be pulled into close contact by capillary attraction (10). These surface forces are a function of particle size and particle size distribution. The larger the particles, the lower the surface forces and the easier it is to disperse the aggregates (11). Small particles cause bridging between large particles and occupy gaps and pores making them less accessible to the vehicle with consequent poor wetting and poorer dispersibility. Similarly, pigments with wide particle size distribution have a greater tendency to reagglomerate or flocculate. Although flocculation is caused by formation of loose units that have been wetted, they do adversely affect the coloristic properties of a pigment–vehicle system by decreasing its tinctorial strength.

A wide variety of additives are being used to reduce aggregation or agglomeration and flocculation to improve dispersibility and color strength of organic pigments. These include polymers and resins, especially those related to abietic acid, aliphatic amines, amides, substituted derivatives of pigments themselves, and various combinations thereof. The additives are most effective if they are present when the pigment crystals are being generated.

3.5. Hiding Power and Transparency. Hiding power (opacity) of a pigment is a function of its strength, that is, its absorption coefficients, its particle size, or light-scattering coefficient, and relative refractive indexes of pigment and vehicle. Light scattering has a powerful influence on opacity and, as is seen from Figure 1, it goes through a maximum as a function of particle size. The maximum occurs at a particle size which is approximately one-half of the wavelength of absorbed vis light.

Similarly, a pigment that absorbs much light increases hiding even when light scattering is insufficient, and the higher the refractive index the greater the hiding power of a pigment. In practical systems hiding is determined by the ability of a pigment dispersion to completely hide or cover up a black and white checkered board.

Conversely, to increase transparency light scattering must be minimized by particle size reduction. The smaller the particle size and the better the dispersion the greater the transparency. Upon continued particle size reduction of a pigment, tinctorial strength comes to a maximum but transparency continues to increase. Transparent coatings are important in multicolor printing as well as metallized finishes, particularly in the automotive industry. Transparency is determined by the contrast ratio obtained from reflectance measurements of a pigmented system applied on a black and white background.

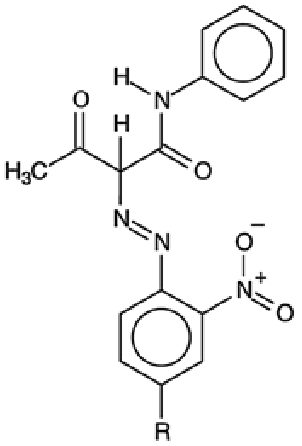
3.6. Other Working Properties. Other properties that facilitate pigment incorporation and use include compatibility with a system, oil absorption, rheological characteristics, gloss, distinctness of image, wettability, migration fastness, plate-out, polymer distortion, etc. Most of these properties are controlled during pigment manufacture or formulation, others require special treatments to overcome undesirable effects. Pigments vary widely in most properties but the requirements for various systems also vary. For example, pigments used in red inks for printing comic books differ vastly from those used in red automotive top-coatings.

4. Types of Pigments

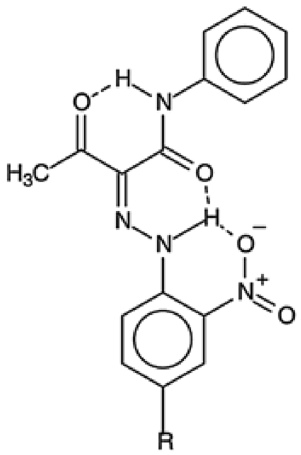
All organic pigments have to be synthesized and nearly all have to be conditioned or finished. The physical conditioning is often as important as its chemical constitution. This is particularly well illustrated by comparing the appearance of crude copper phthalocyanine with pigmentary material. The difference in tinctorial strength is profound, brought about by the conditioning process which most importantly affects particle size and shape and other characteristics of the particle surface. Pigment conditioning has become an important separate process step in organic pigment manufacture.

4.1. Azo Pigments. Azo pigments provide good examples of materials in which conditioning is an integral part of the synthesis process. The coupling process for azo components is simple. An aromatic amine is diazotized by treatment with nitrous acid under conditions which vary from dilute mineral acid to concentrated sulfuric acid, depending on the basicity of the amine (see AZO DYES). The resulting ice-cold diazo solutions are then mixed with finely divided coupling components which comprise a wide variety of chemical types, eg, 2-naphthol, 3-hydroxy-2-naphthoic acid and its arylamides, arylamides of acetoacetic acid, pyrazolone derivatives, etc. Cooling is accomplished by adding crushed ice, and heating by introducing live steam. The simplest method, ie, direct coupling, involves running the diazo solution directly into the solution or suspension of the coupling component or components. In reverse coupling, the coupling component is run into the diazo solution. The most elegant technique, simultaneous coupling, entails running both the diazo and coupling component simultaneously into water or a dilute buffer. This method allows careful control of the pH, as well as other important variables of temperature, rate of coupling, use of auxiliary agents, etc. The latter are of particular importance since they frequently affect rate of nucleation and control particle size, dispersibility, and other pigmentary properties of the resulting products that range in color essentially over the entire visible spectrum.

The monoazo and disazo pigments contain one or more chromophoric groups usually referred to as the azo (–N=N–) group. However, it has been shown by X-ray diffraction analysis and nuclear magnetic resonance (nmr) techniques that azo pigments, eg, the following, where R = H, Cl, or CH_3, exist in the hydrazone rather than the azo tautomeric form (12a,b). The hydrazone form, shown below, which has three intramolecular hydrogen bonds, renders the molecule planar (with the exception of the aniline moiety) which is a stabilizing influence. Similar studies in the Naphthol AS series have shown that the hydrazone rather than the azo form is the prevalent tautomer (13a).



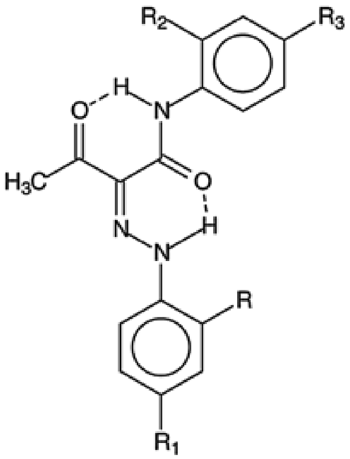
Azo form



Hydrazone form

Azo pigments, one of the oldest and most diverse group of pigments, comprise two types. One type consists of pigments that are insoluble in the aqueous reaction medium in which they are synthesized, eg, Hansa and diarylide yellows and oranges, or arylide reds and maroons. Most of the pigments show poor bleed characteristics, but relatively good acid and alkali resistance. They show acceptable lightfastness in deep shades but poor tint lightfastness. The second type are laked or precipitated azo pigments derived from components substituted with sulfonic and/or carboxylic acid groups. The pigments are rendered insoluble by precipitation as calcium, barium, strontium, or manganese salts. Among the commercially important laked pigments are calcium Lithol Red [1103-39-5] and Lithol Rubine [5281-04-9], Lake Red C [5160-02-1], calcium Red 2B [7023-61-2], and more recently introduced yellows based on pyrazolone sulfonic acid derivatives. These pigments are characterized by good to excellent bleed resistance, poor acid and alkali resistance, fair to good lightfastness in deep shades, and poor tint lightfastness. Also available are special azo pigments which show very good overall properties and therefore find applications in fairly demanding systems.

4.2. Monoazo Pigments. Monoazo yellow pigments are represented by the following general formula:

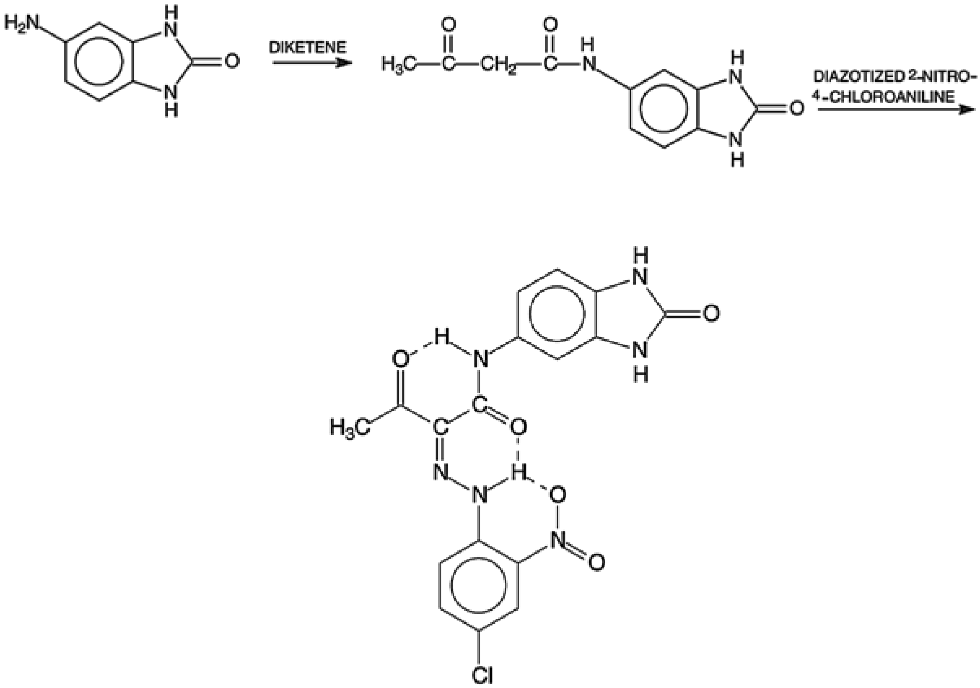


Many of the pigments carry a nitro group in the diazonium component, usually in the ortho position ($R = NO_2$). Among the acetoacetarylide components the *o*-methoxy derivative ($R_2 = OCH_3$, $R_3 = H$) is one of the most important in the production of azo pigments. The colors of these pigments range from red to green-shade yellows. Commercially important products are shown in Table 3.

The most important of these in terms of commercial sales is P.Y. 74, which is relatively strong and the color varies as a function of particle size from green shade to red shade yellow. The larger the particle size the redder the hue and the better the lightfastness.

These pigments are sensitive to heat and bleed in most paint solvents. They are, however, resistant to acids and bases. Their tinctorial strength is considerably greater than that of inorganic yellows but they are weaker than the diarylide yellows. They are used extensively in emulsion paints, paper coating compositions, inks (qv), and, depending on particle size, can in some cases be used outdoors because of very good lightfastness in full shades.

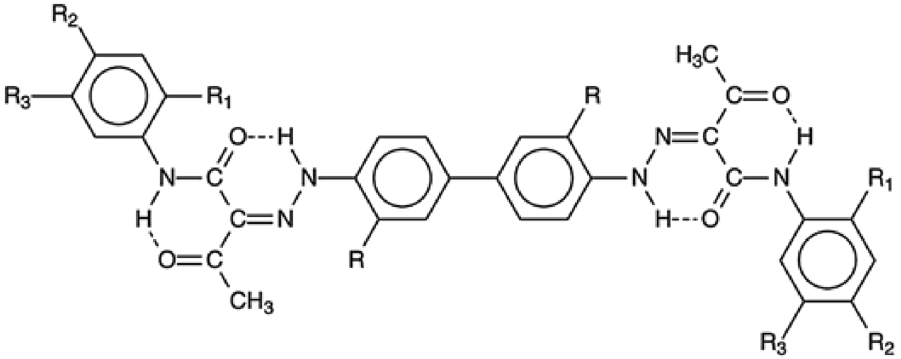
4.3. Benzimidazolones. This class of pigments derives its name from 5-aminobenzimidazolone [95-23-8], which upon reaction with diketene or 2-hydroxy-3-naphthoyl chloride leads to compounds that can be coupled with a variety of diazotized amines.



PO 36

The acetoacetarylides yield yellow to orange pigments and the naphthoic acid amides yield red and brown pigments. Because of the considerable insolubility of the generated pigments they usually require a special thermal aftertreatment to grow crystals to a useful pigmentary range. Pigment Yellow 154 [63661-02-9], derived from coupling diazotized 2-trifluoromethylaniline, and Pigment Orange 36 [12236-62-3] from 2-nitro-4-chloroaniline with 5-acetoacetylaminobenzimidazolone, are among a series of pigments that have found application throughout the paint industry for a variety of industrial finishes and in some plastics applications. The excellent properties of the benzimidazolone pigments are explained not only by the intramolecular but also the extensive intermolecular hydrogen bonding as shown by single-crystal X-ray diffraction studies (13b).

4.4. Diarylide Yellows. Diarylide or disazo yellow pigments are represented by the following general structural formula:



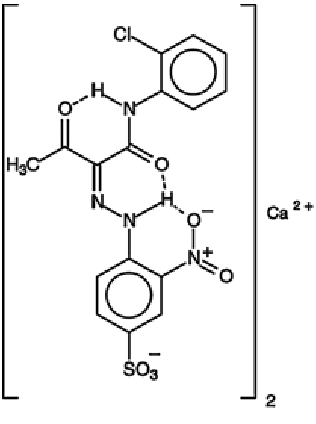
The chemistry and process of manufacture are very similar to the monazo pigments, except a diamine, usually 3,3′-dichlorobenzidine, is tetrazotized and then coupled with two equivalents of an acetoacetarylide. In some cases, two different arylides are used, leading to a mixture of three compounds which enhance tinctorial strength and extend the range of available pigments.

Diarylides show significantly greater tinctorial strength and superior bleed and heat resistance than the conventional monoazo pigments. However, they are generally inferior to the monoazo pigments in lightfastness.

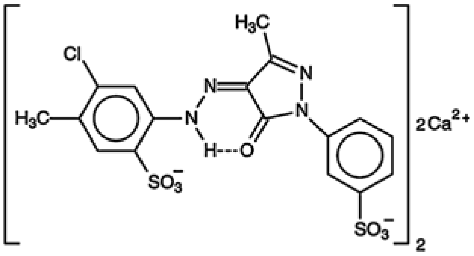
Base-soluble resins are frequently coprecipitated with diarylides without proportional diminution in the strength and a significant increase in transparency of the resulting pigments. Based on high strength and versatile transparency most of the arylides are used in a variety of printing inks, and in some plastics where temperature restrictions of 200°C have been imposed (14). Some commercially important products are shown in Table 4.

Unlike most diarylide yellows, Yellow 83, a reddish yellow, possesses very good lightfastness particularly in its opaque form and consequently is used in plastics and paints in addition to inks.

4.5. Monoazo Yellow Salts. Several monoazo yellow salts have gained popularity since the 200°C temperature restriction on the use of diarylide yellows has been imposed. One is Pigment Yellow 168 [71832-85-4], the calcium salt of diazotized 3-nitro-4-aminobenzenesulfonic acid coupled with acetoacet-2-chloroanilide. It provides a clean, somewhat greenish yellow color that shows good migration resistance but relatively poor tinctorial strength. It is used in polyethylene and inexpensive industrial finishes where the durability requirements are not high.



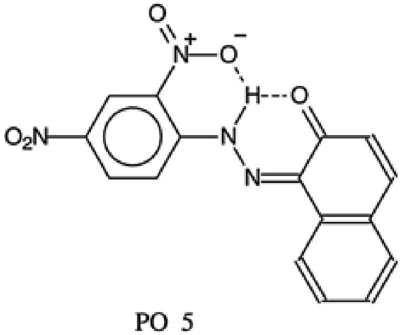
PY 168



PY 191

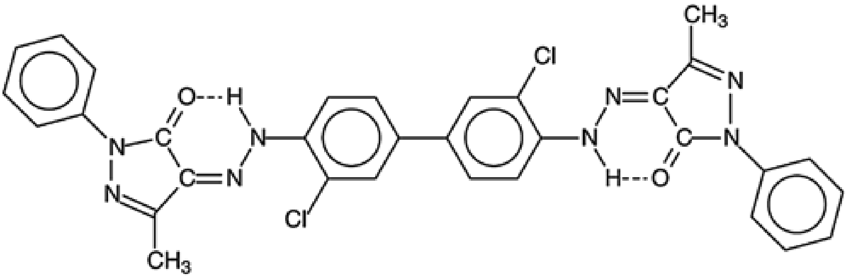
A second example is the yellow pyrazolone salt, Pigment Yellow 191 [129423-54-7]. It is the calcium salt of diazotized 2-amino-4-chloro-5-methylbenzenesulfonic acid coupled with 3-methyl-1-[3′-sulfophenyl]-5-pyrazolone and provides a reddish yellow pigment for use in plastics applications. It shows very good heat stability and excellent resistance to nonpolar solvents and commonly used plasticizers (qv). It finds applications in high density polyethylene, polystyrene, and ABS, and shows satisfactory lightfastness.

4.6. Dinitraniline Orange. Dinitraniline Orange or Pigment Orange 5 [3468-63-1] is a strong and bright orange pigment with relatively low hiding power and good lightfastness in full shades, but poor tint lightfastness. It shows poor bleed but acceptable base resistance and finds principle application in air-drying systems, including a variety of printing inks.



PO 5

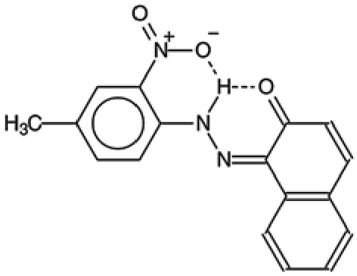
4.7. Pyrazolone Orange. Pyrazolone Orange or Pigment Orange 13 [3520-72-7] is a disazo pigment of high strength and bright color with good lightfastness in full shades and poor tint lightfastness. It is characterized by fair base and chemical resistance and is used primarily in inks, with limited application in paints and plastics.



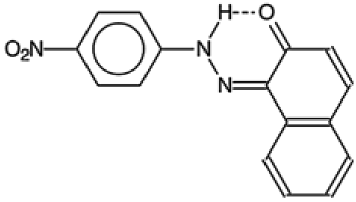
PO 13

4.8. Azo Reds and Maroons.

Toluidine Red. Pigment Red 3 [2425-85-6] is a popular organic red pigment used in industrial finishes. Its hue varies considerably with particle size and therefore several shades are commercially available. In full shade the pigment is very lightfast and weatherfast but shows poor tint lightfastness. It is characterized by poor fastness toward solvents and is likely to bloom in baking enamels. Its principal application is in air drying paints, and to a limited extent in printing inks.



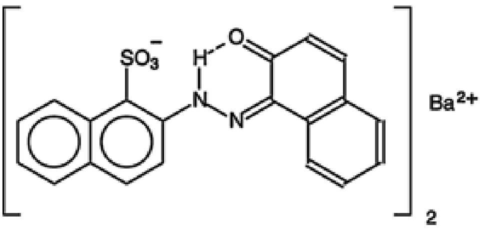
PR 3



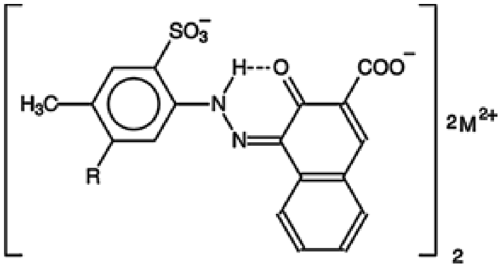
PR 1

Para Reds. Para Red or Pigment Red 1 [6410-10-2] is an intense, reasonably opaque red which shows poor lightfastness, particularly in tints. The pigment is bluer than Toluidine Red. The related pigment Parachlor Red (Pigment Red 4 [2814-77-9]), derived from 2-chloro-4- nitroaniline, is an intense yellowish red. Both pigments show poor bleed and bake resistance and a tendency to bloom in enamels. The pigments are used in some inks and in low cost articles such as detergents, floor polishes, colored pencils, etc. The use of these pigments has declined markedly as a result of greater quality demands by the coatings industry.

Lithol Reds. Lithol Red or Pigment Red 49:1[1103-38-4] is one of the most important of the precipitated salt pigments. They comprise a family of sodium (PR 49), barium (PR 49:1), calcium (PR 49:2), and strontium (PR 49:3) salts of diazotized Tobias acid (2-naphthylamine-1-sulfonic) acid coupled with 2-naphthol. The most popular are the barium and calcium salts, the former being yellower in shade. These reds are used where brightness, bleed resistance, and low cost are of primary importance. They are neither resistant to heat nor chemicals, and are used primarily in printing inks and some inexpensive air-dried industrial paints where good durability is not required.



PR 49:1



PR 57:1 (R = H; M = Ca)
PR 48 (R = Cl)

BON Reds and Maroons. The BON or BONA Reds and Maroons derive their name from β-hydroxynaphthoic acid, also known as 3-hydroxy-2-naphthoic acid [92-70-6]. BON is used as a general coupling component for the entire group with various diazotized amines containing salt-forming groups. Insolubilization is effected by precipitating calcium, barium, strontium, or manganese salts. Colors vary from yellowish red to dark maroon.

Lithol Rubine. Lithol Rubine (Pigment Red 57:1 [5281-04-9]), also referred to as 4B toner, is the calcium salt of diazotized 2-amino-5-methylbenzenesulfonic acid coupled with 3-hydroxy-2-naphthoic acid. It ranks high among organic pigments in production volume and use.

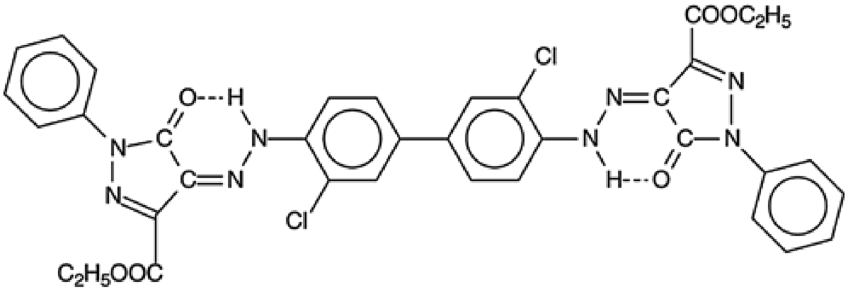
The probable crystal structure of PR 57:1 has been investigated by solid state NMR. A combination of techniques inferred a polymeric sheet-like structure in which the divalent cation is associated with the anionic carboxy and sulfonate groups from different pigment molecules (12b). By implication this type of molecular packing probably applies to many other similar pigments.

Lithol Rubine is characterized by high tinctorial strength, good bleed, and bake resistance but poor alkali, soap, and acid resistance. Its lightfastness is considered fair and varies within a wide range of shades obtained by inclusion of auxiliary agents. Because the pigment is brighter than Lithol Reds, it is used extensively in oil, gravure, and flexographic inks. It is heat stable up to ~250°C and is therefore a suitable candidate for indoor use in polyethylene and spin-dyed polypropylene. It is also used extensively in cosmetic applications.

Red 2B. Red 2B defines the important barium (PR 48:1 [7585-41-3]), strontium (PR 48:3), calcium (PR 48:2), and manganese (PR 48:4) salts of diazotized 2-amino-4-chloro-5-methylbenzenesulfonic acid coupled with 3-hydroxy-2-naphthoic acid. The first three are bright red pigments, becoming bluer in that sequence. They exhibit high strength, good bleed, and bake resistance, but poor resistance to alkali, soap, and acids, and fair lightfastness. The main fields of application are printing inks, plastics, and inexpensive industrial paints.

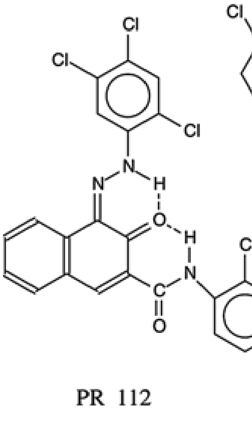
Manganese 2B (PR 48:4) is a bluish red, characterized by superior masstone lightfastness and outdoor durability, and finds use in some automotive and other high quality industrial finishes. It is also used in some plastics, because of reasonably good heat stability, and a variety of printing inks.

Pyrazolone Reds. The pyrazolone reds are disazo pigments which provide high color strength and reasonable lightfastness in full shades but poor tint lightfastness, good bake, bleed, and chemical resistance. Some find application in plastics such as poly(vinyl chloride) (PVC), where they show good dielectric properties, making them useful for cable insulations, in rubber, and specialized printing inks. Pigment Red 38 [6358-87-8] is the product obtained by coupling diazotized 3,3^1-dichlorobenzidine with *N*-phenyl-3-carbethoxy-5-pyrazolone.

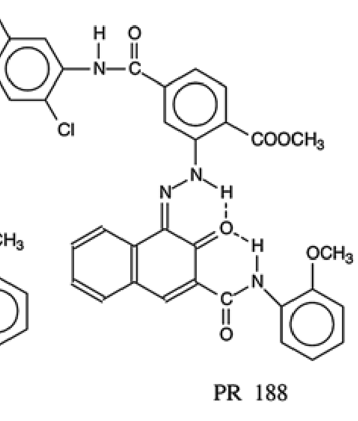


PR 38

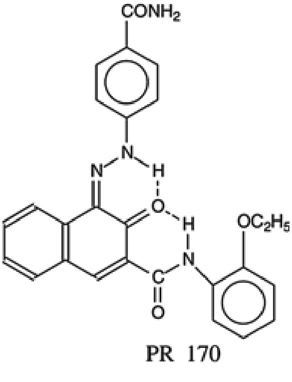
4.9. Naphthol Reds and Maroons. Naphthol Reds and Maroons are monoazo pigments which provide a wide range of colors from yellowish and medium red to bordeaux, maroon, and violet, and are characterized by high strength but marginal migration resistance. Depending on the substitution pattern some are strongly migrating and others are more or less resistant to migration. The introduction of amide functions, in addition to the arylamide of 3-hydroxy-2-naphthoic acid on which all of this type of pigment are based, provides a measure of migration improvement. Lightfastness is generally marginal to good. Pigment Red 112 [6535-46-2] is a brilliant medium red pigment, approaching the shade of Toluidine Red, which is used in a variety of printing inks, air drying, and emulsion paints.



PR 112



PR 188



PR 170

Another important member of this class is Pigment Red 188 [61847-48-1] derived from a substituted aminoamide and arylamide of 3-hydroxy-2-naphthoic acid. It is an intense yellowish shade red pigment with good fastness properties. Its main field of application is in inks using a variety of printing techniques, and in paints. The prints are very fast to organic solvents, soap alkali, and acids.

Still another important pigment in this class is Pigment Red 170 [2786-76-7)], which provides medium shades of red, and when particle-grown produces an opaque modification that shows improved migration resistance and lightfastness. Like some other Naphthol AS pigments it shows the phenomenon of polymorphism. It is used in high grade industrial paints and, in combination with high performance pigments, in automotive finishes. The transparent type, which is tinctorially strong, finds applications in a variety of printing inks.

4.10. Azo Condensation Pigments.

A further improvement in heat stability of azo pigments was achieved by the condensation disazo pigments due to an enlarged molecular framework and higher molecular weight. Formally they are composed of two monoazo or more accurately two monohydrazone units, which are attached to each other by an aromatic dicarbonamide bridge. Both red and yellow pigments are prepared by essentially the same or modified processes. The red group of pigments is synthesized by coupling 3-hydroxy-2-naphthoic acid with a diazotized amine, followed by conversion to the acid chlorides and diamide formation by reaction with aromatic diamines. An example is Pigment Red 144 [5280-78-4] (Fig. 2a).

The yellow members of this pigment class are obtained by coupling a diazotized aminobenzoic acid with a bisacetoacetarylide, followed by conversion to a diacid chloride and reaction with a substituted aromatic amine. An example is Pigment Yellow 93 [5580-57-4] (Fig. 2b).

The pigments are used primarily in plastics, including polypropylene fibers, because of very good bleed resistance, heat stability, and lightfastness. The reds also find use in printing inks, primarily for high quality products.

4.11. Lakes.

Lakes are either dry toner pigments that are extended with a solid diluent, or an organic pigment obtained by precipitation of a water-soluble dye, frequently a sulfonic acid, by an inorganic cation or an inorganic substrate such as aluminum hydroxide.

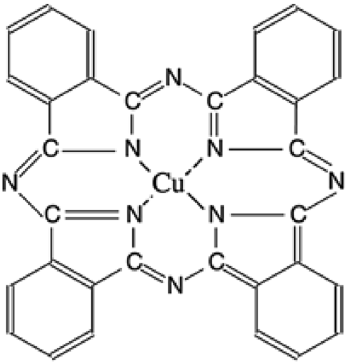
Basic dyes are characterized by bright shades and high strength but poor lightfastness. However, when laked by precipitation with soluble salts of organic acids such as tannic acid, or inorganic heteropolyacids like phosphotungstic (PTA) and

$$\begin{array}{ccc} \mathrm{H_3[P(W_3O_{10})_4]}x\mathrm{H_2O}\ amp & \mathrm{H_3[P(Mo_3O_{10})_4]}x\mathrm{H_2O}\ amp & \mathrm{H_3[P(Mo_3O_{10})_3(W_3O_{10})]}x\mathrm{H_2O} \\ \text{PTA}\ amp & \text{PMA}\ amp & \text{PTMA} \end{array}$$

phosphomolybdic (PMA), and the combined phosphotungstomolybdic acid (PTMA), the resulting pigments retain the dyes' tinctorial attributes, but become insoluble and show improved lightfastness. Ideally three acidic hydrogens can be replaced by three dye molecules to form pigments that are characterized by uncommonly clean and brilliant red and violet shades. They are, however, not stable to polar solvents or alkali and fail to satisfy stringent fastness requirements, particularly in packaging and special inks. Representative basic dyes that are converted to pigments by complex formation are listed in Table 5.

4.12. Copper Phthalocyanines. Copper phthalocyanine [147-14-8] (CPC, Pigment Blue 15) approximates an ideal pigment. This class of pigments offers extreme brightness, tinctorial strength, bleed and chemical resistance, stability to heat, and migration. The pigments show excellent weatherfastness but are restricted to the blue and green regions of the spectrum. Phthalocyanine blue and green are among the most important organic pigments on the worldwide market.

Copper Phthalocyanine Blue. CPC blue exists in several polymorphic modifications, two of which, the red-shade blue alpha and green-shade blue beta form, are of great commercial significance. Beta is the thermodynamically more stable phase and is the product resulting from manufacture by the two basic processes using either phthalonitrile or phthalic anhydride as starting materials, either in the presence of a solvent or by a dry baking process. The alpha form is usually obtained by conversion from the beta form and has to be stabilized to prevent phase reconversion. The pronounced tendency of the alpha form to flocculate in fluid media is suppressed by special surface treatments and/or the introduction of a small amount of aromatically bound chlorine to form solid solutions between CPC and its chlorinated derivatives. A so-called semichloro-CPC containing an average of ~ 0.75 chlorine atoms per molecule provides a stable pigment even upon incorporation in high temperature plastics.



PB 15

Despite the superficially structural complexity of the CPC molecule, it is prepared with comparative ease (16) (see PHTHALOCYANINE COMPOUNDS). The preferred manufacturing process starts with phthalic anhydride and is carried out in a variety of solvents, trichlorobenzene having been the preferred solvent, but it has been replaced with high boiling hydrocarbons or glycols in order to avoid the formation of the hazardous and poorly degradable polychlorinated biphenyls.

The coarse, nonpigmentary crudes are particle size reduced by a variety of processes to obtain pigmentary CPC. Since CPCs are utilized in a variety of industries and a host of applications, the specific property requirements vary widely. A large number of special-purpose types are commercially available designed to provide optimal properties for specific applications.

Copper Phthalocyanine Green. CPC green is obtained by electrophilic substitution of CPC blue with chlorine, the degree of chlorination reaching 14–15 chlorines per molecule. The typical polychloro-CPCs are blue-shade green pigments, such as PG 7 [1328-53-6]. To provide yellower shades of green, substitution of bromine for chlorine with up to eight or nine bromine atoms per molecule, the rest being chlorine, is carried out. A typical example is PG 36 [14302-13-7]. Like CPC blue the green pigments show outstanding pigmentary properties, but are lower in tinting strength with progressive halogen substitution, particularly with bromine.

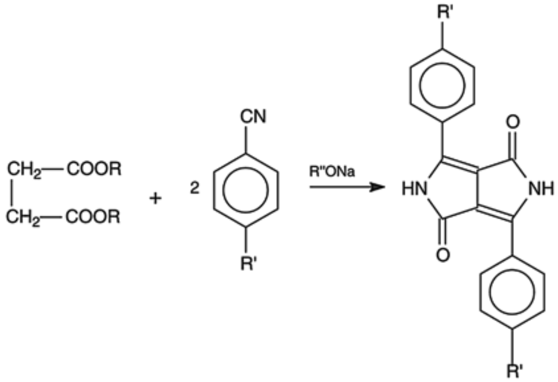
4.13. Quinacridones.

Quinacridone pigments offer generally outstanding fastness properties across the visible spectrum from red-shade yellows to scarlet, maroon, red, magenta, and violet (17). The pigments are practically insoluble in most common solvents, and therefore show excellent migration resistance in most application media. The low solubility is attributed to effective intermolecular hydrogen bonding (18), which is also responsible for the photochemical stability. The various available colors are the result of polymorphism and various substitution patterns. The parent compound Pigment Violet 19 [1047-16-1] exists in three polymorphic modifications. The red gamma and violet beta forms are commercial pigments, whereas the red alpha form is metastable. The pigments are synthesized by two principal processes; both involve the common intermediate dimetyl 2,5-diarylamino-3,6-dihydroterephthalate (I in Fig. 3). Substitution in the 2,9-positions of quinacridone leads to magenta pigments, whereas 4,11-substitution causes shifts to shorter wavelengths and scarlet or orange pigments. Oxidation of quinacridone (II in Fig. 3) yields quinacridonequinone (QAQ), a yellow pigment which, like the 4,11-disubstituted pigments, is not lightfast. However, in solid solutions with quinacridone, pigments of excellent durability are obtained. Both opaque large particle size and transparent particle size-reduced pigments are commercially available. Table 6 lists some commercial products.

Due to excellent pigmentary properties, quinacridones are used in many industries but particularly in automotive finishes, emulsion paints, plastics, and fibers.

4.14. Diaryl Pyrrolopyrroles.

The 1,4-diketo-3,6-diarylpyrrolo(3,4-*c*) pyrroles are the most recently discovered class of pigments ranging in color from orange to bluish red. The pigments are synthesized by base-catalyzed condensation of higher dialkyl esters of succinic acid with aromatic nitriles. One important member of this class is Pigment Red 254, which is a very opaque yellowish red pigment of outstanding durability, brightness, and chemical resistance. Another is Pigment Red 264, which is a high performance rubine pigment. Other analogs have been commercialized (see Table 7), which have broadened the color palette of this important pigment class. These pigments are used primarily in automotive finishes, plastics, fibers, and inks.



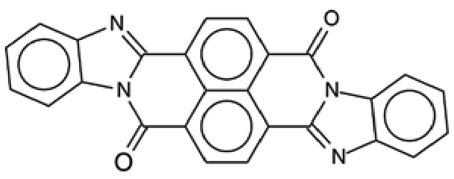
4.15. Vat Dye Pigments. Vat dyes have been used for a long time for coloring textile fibers. As pigment technology evolved with a variety of physical and chemical methods for conditioning or finishing pigments, they were also successfully applied to largely insoluble dyes. Improved purity of products coupled with optimized particle size and particle size distribution has afforded pigments of considerable commercial interest. Only a few of the very large number of vat dyes have found application in the pigment field.

Perylenes. Perylene pigments are either the 3,4,9,10-tetracarboxylic dianhydride or more often N,N′-substituted diimides (Table 8).

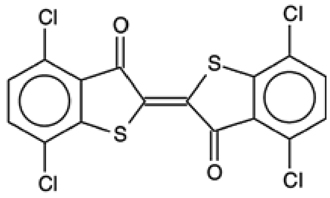
The pigments are manufactured either by reaction of the dianhydride with an amine or *N,N′*-dialkylation of the diimide. They are characterized by high tinctorial strength, excellent solvent stability, very good weatherfastness, moderate brightness, and range in color from red to violet. An exception is the dianhydride that is not stable to alkali.

Most applications are in high grade industrial paints, especially automotive finishes. Some types (PR 149) are used primarily in plastics and fibers.

Perinones. The most important pigment in this family is the orange perinone, Pigment Orange 43 [4424-06-0], which is obtained by reaction of naphthalene-1,4,5,8-tetracarboxylic dianhydride with *o*-phenylenediamine. The result is a mixture of the cis and trans isomers. The commercial product is the orange trans compound that must be separated from the dull, bluish red cis isomer, and then conditioned for pigment use. The pigment is fairly weatherfast and heat stable, and is used primarily in plastics and fiber applications.



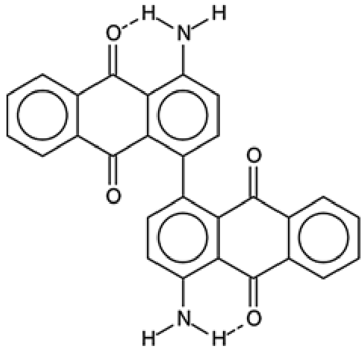
PO 43



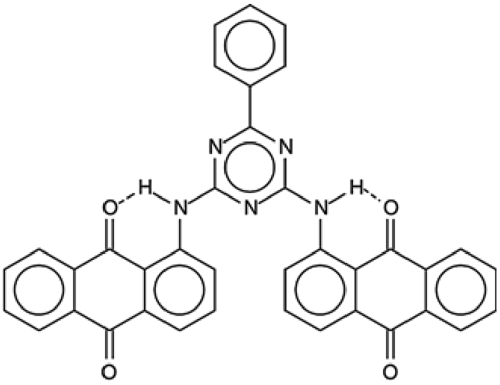
PR 88

Thioindigo. Thioindigo pigments are produced by oxidative dimerization of variously substituted thioindoxyls or thionaphthenones. The most important pigment in this series is Pigment Red 88 [14295-43-3] a red-violet pigment in which the chlorine substituents are essential to confer marginal to acceptable lightfastness and stability to solvents. Although still used in some paint and plastic systems, it is being replaced by pigments of higher quality.

4.16. Aminoanthraquinone Pigments. Pigment Red 177 [4051-63-2] has the chemical structure of 4,4′-diamino-1,1′-dianthraquinonyl and is prepared by intermolecular copper-catalyzed debromination of 1-amino-4-bromoanthraquinone-2-sulfonic acid followed by desulfonation. It is the only known pigment with unsubstituted amino groups that are involved in both intra- and intermolecular hydrogen bonding (20). The bluish red pigment is used in plastics, industrial and automotive paints, and specialized inks (see DYES, ANTHRAQUINONE).



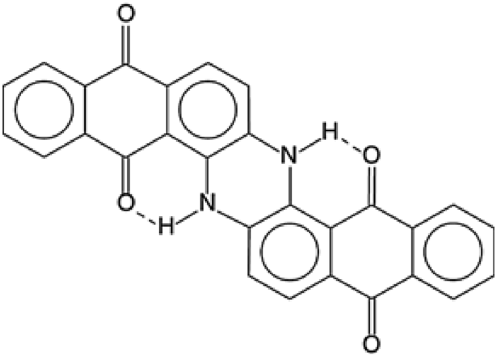
PR 177



P.Y. 147

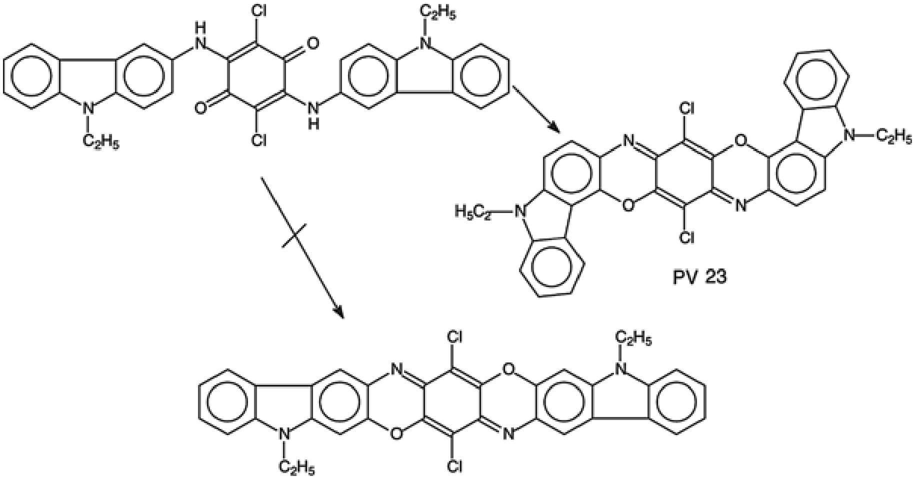
Pigment Yellow 147 [4118-16-5] is derived from reaction of 1-amino-anthraquinone with 1-phenyl-3,5-dichloro-2,4,6-triazine. It is a reddish shade yellow pigment used primarily in certain plastics and in polyester and polypropylene fibers.

Indanthrone. Pigment Blue 60 [81-77-6] is synthesized by oxidative dimerization of 2-aminoanthraquinone in the presence of a strong base, and then particle size reduced by precipitation from very strong sulfuric acid or by milling. The very red-shade blue pigment shows outstanding weatherfastness in full shade as well as in light white reductions. It is used primarily in metallized automotive finishes where it shows weatherfastness comparable to copper phthalocyanine blue.

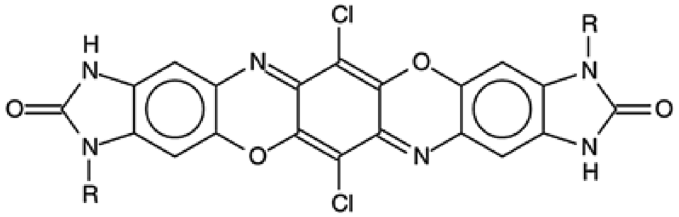


PB 60

4.17. Dioxazines. Carbazole Violet (Pigment Violet 23 [6358-30-1]) is synthesized by reaction of chloranil with 3-amino-*N*-ethylcarbazole followed by oxidative acid-catalyzed thermal cyclization, and conditioniong via milling or acid treatment. Since its discovery in the 1950s the linear structure had been assigned to this pigment. It has now been established that the cyclization goes in an angular fashion, and that the unequivocally synthesized linear compound is different from PV 23 (21). The bluish violet pigment is uncommonly strong, resistant to some solvents, and shows good weatherfastness. It is used primarily as a shading pigment with copper phthalocyanines and for toning whites in a variety of systems.



A new linear, substituted analogue of triphendioxazine, Benzimidazolone Dioxazine (PB 80) has recently been described (22). It contains the same basic structural framework present in PV 23, but annealed to the peripheral benzene rings are two imidazolone moieties.

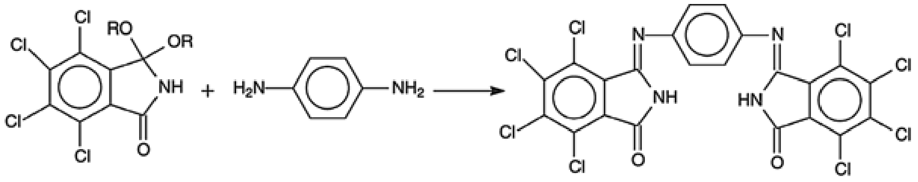


$R = CH_3$ or C_2H_5

PB 80

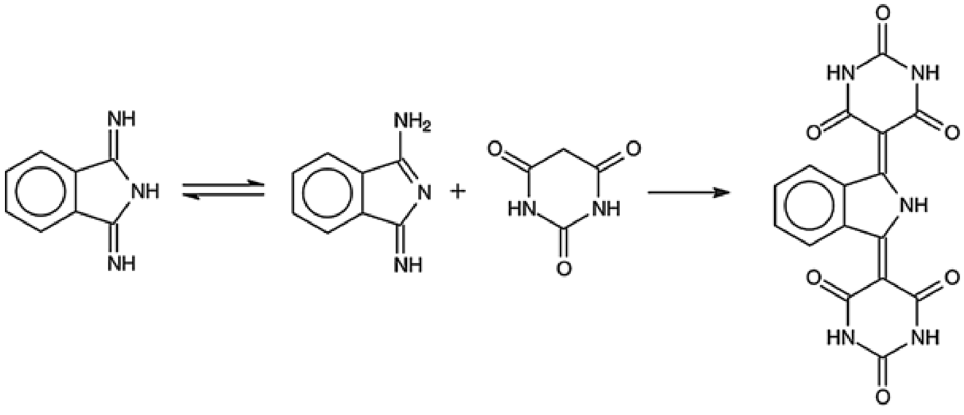
The structural modification imparts greater insolubility, while preserving, in fact enhancing, the strength of the chromophore. The color of the pigment falls about half way between PB 60 (Indanthrone Blue) and PV 23 (Carbazole Violet). It shows excellent heat stability, and sufficient outdoor durability to qualify it as a high performance pigment. The pigment has been introduced commercially.

4.18. Isoindolinones and Isoindolines. Tetrachloroisoindolinone pigments are synthesized by condensation of 3,3,4,5,6,7-hexachloroisoindoline-1-one or the corresponding 3,3-dialkoxy derivatives with aromatic diamines yielding pigments ranging in color from green-shade yellows to oranges. The pigments are characterized by very good lightfastness, heat stability, migration resistance, and chemical inertness. Although Pigment Yellow 110 [5590-18-1], a red-shade yellow, is relatively weak, it finds extensive use in automotive and other high grade finishes and in a variety of plastics and ink applications.



PY 110

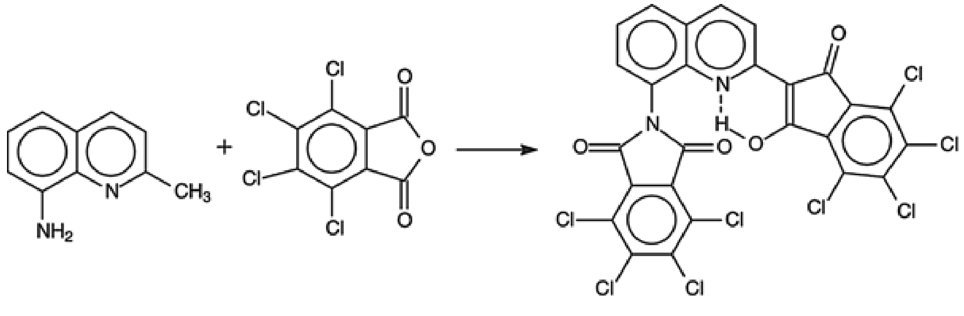
Isoindoline pigments are synthesized by reaction of 1-amino-3-iminoisoindolenine(diiminoisoindoline) with 2 mol of compounds containing activated methylene groups. In Pigment Yellow 139 [36888-99-0] the second component is barbituric acid. PY 139 is a reddish yellow pigment that differs in color as a function of particle size. The opaque version is the reddest. The pigment is lightfast but tends to darken in full shades. Although marginal in chemical resistance the pigment is used in the paint and plastics industries.



PY 139

4.19. Quinophthalones.

The quinophthalone pigments are prepared by condensation of quinaldines with a variety of aromatic anhydrides. Introduction of a hydroxyl group in the 3-position of quinaldine yields yellows of improved lightfastness. One important pigment in this series, shown below, Pigment Yellow 138 [30125-47-4], is a reasonably weatherfast greenish yellow pigment of good heat stability. The main field of application is paints and plastics.



PY 138

5. Production and Economic Aspects

At the end of 2003 the four principal producers and/or importers of organic pigments into the United States are BASF Corporation, Ciba Specialty Chemicals., Clariant Corporation, and Sun Chemical Corporation.

A representative list of smaller producers and/or importers of organic pigments into the United States is given below.

Allegheny Color Corp.	Jeco Pigment (USA), Inc.
Apollo Colors, Inc.	Magruder Color Company, Inc.
CDR Pigments and Dispersions	Max Marx Color Corp.
Daicolor-Pope, Inc.	Organic Dyestuffs Corp. (ORCO)
EC Pigments	Toyo Color America LLC
Engelhard Corp.	United Mineral and Chemical Corp.

These relatively small companies deal mostly in classical pigments and market <10% of high performance pigments consumed in the United States.

In the recent past, there have been several acquisitions and consolidations in the pigment industry. A good example is the 2003 acquisition of the Bayer Corporation U.S. pigment business by Sun Chemical Corporation, a subsidiary of Dainippoon Ink and Chemical, Inc. Most large multinational companies have U.S. manufacturing facilities but are part of global enterprises. For example, Ciba Specialty Chemicals has its headquarters and several manufacturing facilities in Switzerland. The same applies to BASF and Clariant Corporations whose headquarters are located in Europe.

The largest challenge to United States based enterprises comes from Asian competitors, particularly China and India. The foreign companies have an important advantage based on low labor costs. Consequently, American companies aim to utilize the most modern automated and computerized manufacturing facilities and are constantly searching for new and improved pigments which are subject to patent protection. As a consequence, the US market for organic pigments is expanding and is expected to grow 5–6% in coming years (23), baring any unforseen or catastrophic incidents.

The strongest growth is expected in paints and conventional as well as powder coatings, and specialty printing inks, boosted by trends toward higher pigment loadings and rapid growth in radiation curing spurred by the need for drastic reduction in VOC emissions. Above average growth is also expected for plastics applications where more briliant and durable colors are generating greater consumer appeal.

At the end of the last decade Western Europe and North America were still the largest colored pigment consuming regions of the world. The breakdown is as shown in Table 9.

In 1999, the largest markets for organic pigments were in North America (37%) and Europe (31%) which, together with Japan (∼11%) , account for the dominant share of the most profitable high performance pigment market, and nearly 79% of the global demand for organic pigments.

Recent annual global production of organic pigments reached about 249,000 metric tons (4). The largest group consists of azo pigments accounting for well over half the total production, 59%. The specific breakdown by pigment classes is shown in Table 10.

The proportion of polycyclic pigments, belonging mostly to the high performance pigment group, has tended to rise and is currently up to 9% of global pigment production, but by value its share has risen to 26% of the total (5). The four major US based manufacturers and/or importers account for more than 90% of the market value of organic high performance pigments.

It is noteworthy that demand for organic pigments in the United States has risen significantly in recent years and is predicted to continue to increase at essentially the same rate up to year 2010. The increase in demand has overtaken total United States dye demand in terms of value and is expected to be 70% ahead of dye demand in the year 2010. This is detailed in Table 11.

In part, as a consequence of growth in high performance pigments, there was a significant increase in American exports of organic pigments and their preparations in the last 10 years, as detailed in Table 12. In 2002, the total amount of exported pigments versus 1992 rose 87.5%, (40,855 vs. 21,793 metric tons) with an increase in export value of 58.9%.

It is noteworthy that imports into the United States of pigments and their preparations, specified by pigment class in Table 13, also shows a significant increase from 1992 (24) to 2002 (26) amounting to 77.4% (20,891 vs. 37,071 metric tons) while the increase in value amounts to only 17.3% (\$267,722 $\times 10^3$ vs. \$314,137 $\times 10^3$). The importation of relatively inexpensive pigments from abroad is supported by these official statistics.

6. Testing and Standardization

Pigments are subjected to a number of tests before they are released to customers. Testing is complicated because of the great diversity of pigment types and uses. A given pigment may be dispersible in one system but poorly dispersible in another, and can exhibit different durability depending on the system. Performance is system dependent. Standardization is carried out against a standard sample for coloristics and a variety of working properties. Among the tests, depending on the pigment type, may be thermal stability, hiding power, rheology, migration, chemical stability, gloss, distinctness of image, durability, etc. Durability or weatherfastness are usually established for a standard and other samples, which are tested occasionally together by exposure under actual conditions of use. Car paint manufacturers, for example, require exposure in Florida under specific conditions for at least two years. Accelerated exposure under artificial light and simulated weather sequences is also employed, requiring significantly shorter times of exposure. In plastic systems, inks or fibers accelerated exposure is generally an acceptable method of testing. The mechanism of photochemical degradation of organic pigments is not fully understood.

In the process of testing, color deviations are expressed in the CIELAB system which projects total color differences either on the axes of the rectangular Lab or the equivalent polar LCH system (27). In either case tested samples must fall within acceptable ranges or limits established versus a standard by the pigment manufacturer and accepted by the pigment user.

In dispersing a pigment by an established method, acceptable pigment strength versus a standard must be achieved, even though an ideal dispersion normally is never realized, that is, not all agglomerates are broken down completely. In effect, there is more color strength built into a pigment than is usually realized commercially, and the dispersion process is simply discontinued for economic reasons.

7. Health and Safety Factors

Since pigments are generally insoluble, unlike most dyes, they are usually not bioavailable and consequently are generally not absorbed or metabolized. Nevertheless many health-related studies have been carried out and reported in the literature. A summary (28) of rabbit tests with 192 organic pigments showed that six are skin irritants and 24 cause various degrees of eye irritations, the rest being nonirritating.

Acute toxicity of organic pigments has been studied extensively. The most common measure of toxicity is LD_{50} expressed in mg/kg of body weight which has a lethal effect on 50% of test animals after a single (oral, dermal, etc) administration. These tests assess toxicity versus other known compounds. A large LD_{50} value represents a low degree of toxicity. The Federal Hazardous Substances Act defines a material with an LD_{50} above 5000 mg/kg as being nontoxic (29) and the Occupational Safety and Health Administration (OSHA) defines chemicals with an LD_{50} of <500 mg/kg as toxic (30). The Ecological and Toxicological Association of Dyestuffs and Organic Pigments Manufacturers (ETAD) published a summary (31) on toxicity testing of 4000 colorants, the National Printing Ink Research Institute (32) tabulated LD_{50} data for 108 organic pigments, and in a NIFAB symposium lecture (33) the toxicology of 194 pigments was reviewed. Most oral LD_{50} values exceeded 5000 mg/kg; only four pigments showed values between 2000 and 5000 mg/kg acute toxicity. By OSHAs definition none of the tested pigments are toxic and an overwhelming number are not as toxic as table salt which has an LD_{50} of 3000 mg/kg. Thus, pigments in general have very low levels of acute toxicity.

Chronic toxicity defines a specific dose or exposure level that will produce measurable, long-term toxic effects, including carcinogenicity. Some cancers are thought to arise due to mutations in body cells. Although the correlation between the Ames mutagenicity test (34) and carcinogenicity is a controversial issue it is nevertheless considered to be a useful tool. Out of 24 pigments given the Ames test (35), only two (PO 5 and PR 1) showed weakly positive results. Eleven pigments (PY 12, 16, 83; PO 5; PR 3, 4, 23, 49, 53:1, 57:1; and PB 60) were tested for carcinogenicity by long-term feeding studies. Results (38) were negative for most and equivocal for three (PO 5 and PR 3 and PR 23).

One area that requires special comment is a study (14) that showed that certain diarylide pigments processed in polymers above 200°C and particularly >240°C decompose to give off 3,3′-dichlorobenzidine, an animal carcinogen. As a consequence diarylide pigments (not, however, condensation disazo pigments) are not recommended for use in any applications where they might be exposed to temperatures >200°C.

The hazards associated with handling pigments are contained in the MSDS mandated by an OSHA Hazards Communication Standard (35), which also requires labeling and employee information and training. In addition, pigments that come in indirect contact with food in the packaging industry require special approval from the Food and Drug Administration (FDA).

7.1. Ecological Effects.

The starting materials for manufacture of organic pigments are as diverse as the pigments themselves. However, most starting materials are derived from petroleum or natural gas sources. Although many pigments are synthesized in water, a variety of organic solvents are also employed by the industry. The effective utilization of all starting materials and solvents, and reduction of undesirable by-products, is a primary objective of the organic pigment industry because the cost of environmental protection has increased significantly. Notwithstanding the increasing demand for organic pigments, particularly high performance pigments, the need for replacement of heavy-metal inorganic pigments by acceptable organic substitutes, and the continued demand for brighter and more durable pigments in critical applications, the industry strives to accomplish the task with minimum adverse effect on the ecology while continuing its contribution to the aesthetic side of human existence.

8. Uses

Organic pigments are used for decorative and/or functional effects. In paints, for example, pigments provide color and contribute to exposure durability of the systems, which is particularly true for high performance pigments. Other functional effects include hiding power and high visibility, such as is displayed with daylight fluorescent pigments; the latter are mostly fluorescent dyes dissolved in synthetic resins and are therefore not particularly lightfast. They are used in various printing processes for textiles, plastics, and safety markings of various types (see LUMINESCENT MATERIALS, FLUORESCENT PIGMENTS (DAYLIGHT)).

The most important and established use for pigments is the imparting of color to a variety of materials and compositions. Examples are surface coatings for exteriors and interiors of automobiles and houses with oil- or water-based paints, and powder coatings for appliances and metals; wood stains, leather and artificial leather finishes, distempers; printing inks for rotogravure, lithographic, and flexographic systems, including inks for metal plates, foil, wallpaper, food wrappers, and general packaging materials; textile printing inks for clothing, awnings, bookcovers, etc; application for paper, rubber, shoe polish, roofing granules, concrete, and cement; soaps, detergents, synthetic resins, and wax compositions; color coating of fertilizers and seeds; and laundry bluing. Pigmentation of textile fibers, nylon, polypropylene, and cellulose acetate is practiced. Organic pigments are also used for coloring various plastics including PVC, polyethylene, polystyrene, ABS, polycarbonate, etc. Numerous pigments are also incorporated in artists' material, ie, oils, crayons, chalks, colored pencils, and modeling clay.

On a global basis the consumption of pigments by various industries in 2001 is detailed in Table 14.

Innovation in the field of organic pigments is continuing. Combination of organic pigments with pigments generating color by light interference are likely to make inroads into industrial applications, including automotive finishes. Proper pigment surface treatments in combination with appropriate polymeric dispersants that diminish or preclude flocculation of their dispersions in solvent or waterborne systems to provide stronger and glossier finishes and inks are also likely to become more important commercially. Stir-in pigments, that is those requiring little or no dispersive effort, for decorative and industrial coatings as well as inks are likely to become more important. Pigmented coatings and their distribution by industrial sector that may be positively affected by pigment innovations, particulary improvement in flocculation resistance of their paints, are shown in Table 15.

A considerable effort is continuing in substitution of organic pigments for inorganic pigments that contain heavy metals like lead and cadmium in traffic paint and automotive and agricultural machine coatings, particularly in the developing nations, which will inevitably increase the need for organic pigments. Another growth opportunity is associated with an increase in use of ultraviolet and electron beam (uv/eb) cured coatings and inks. In addition, modern fashions require the use of brighter and bolder colors, which dictate the use of organic pigments.

Discovery of totally new pigments or more effective ways of pigment utilization is vigorously pursued by the colored pigment industry.

Some pigments or pigment derivatives have found unorthodox experimental applications as photoconductors for copiers (37) and in a soluble form as medical agents for photodynamic therapy (38) by sensitized generation of singlet oxygen against certain animal and human cancers. These and other newer fields of application are still under active investigation.

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Table 1. **Selected Commercial Synthetic Organic Pigments**

Color index (CI) name	CAS Registry Number	CI constitution number	Pigment class (common name)	Method of preparation
Pigment Yellow 3	[6486-23-3]	11710	monoazo (Hansa Yellow 10G)	coupling diazotized 2-nitro-4-chloroaniline with acetoacet-2-chloroanilide.
Pigment Yellow 12	[6358-85-6]	21090	diarylide	coupling tetrazotized 3,3′-dichlorobenzidine with acetoacetanilide.
Pigment Yellow 13	[5102-83-0]	21100	diarylide	coupling tetrazotized 3,3′-dichlorobenzidine with acetoacet-2,4-dimethylanilide.
Pigment Yellow 74	[6358-31-2]	11741	monoazo	coupling diazotized 2-methoxy-4- nitroaniline with acetoacet-2-methoxyanilide.
Pigment Yellow 83	[5567-15-7]	21108	diarylide	coupling tetrazotized 3,3′-dichlorobenzidine with acetoacet-2,5-dimethoxy-4-chloroanilide.
Pigment Yellow 93	[5580-57-4]	20710	disazo condensation	coupling diazotized 3-amino-4-chlorobenzoic acid with 1,4-bis(acetoacetylamino)-2-chloro-5-methylbenzene, diacid chloride formation, and amidation with 2-methyl-3-chloroaniline.
Pigment Yellow 95	[5280-80-8]	20034	disazo condensation	coupling diazotized 3-amino-4-chlorobenzoic acid with 1,4-bis(acetoacetylamino)-2,5-dimethylbenzene, diacid chloride formation, and amidation with 2-methyl-5-chloroaniline.
Pigment Yellow 110	[5590-18-1]	56280	Isoindolinone	reaction of 3,3′-dimethoxy-4,5,6,7-tetrachloroisoindolinone with p-phenylenediamine.
Pigment Yellow 138	[30125-47-4]	56300	Quinophthalone	condensation of 2-methyl-8-aminoquinoline with tetrachlorophthalic anhydride.
Pigment Yellow 139	[36888-99-0]	56298	Isoindoline	reaction of 1-amino-3-iminoisoindolenine with barbituric acid.
Pigment Yellow 154	[68134-22-5]	11781	monoazo benzimidazolone	coupling diazotized 2-trifluoromethylaniline with 5-acetoacetylaminobenzimidazolone.
Pigment Yellow 168	[71832-85-4]	13960	monoazo (Ca salt)	coupling diazotized 3-nitro-4-aminobenzenesulfonic acid with acetoacet-2-chloroanilide, followed by salt formation.
Pigment Yellow 191	[129423-54-7]	18795	monoazo pyrazolone (Ca salt)	coupling diazotized 2-amino-4-chloro-5-methyl-benzenesulfonic acid with 3-methyl-1-(3’-sulfophenyl)pyrazolone, followed by salt formation.

Pigment Orange 5	[3468-63-1]	12075	monoazo (Dinitraniline Orange)	coupling diazotized 2,4-dinitroaniline with 2-naphthol
Pigment Orange 13	[3520-72-7]	21110	disazo pyrazolone (Pyrazolone Orange)	coupling tetrazotized 3,3′-dichlorobenzidine with 1-phenyl-3-methylpyrazolone
Pigment Orange 36	[12236-62-3]	11780	monoazo benzimidazolone	coupling diazotized 2-nitro-4-chloroaniline with 5-acetoacetylamino-benzimidazolone
Pigment Orange 43	[4424-06-0]	71105	Perinone	condensation of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride with *o*-phenylenediamine, and separation of trans isomer
Pigment Orange 73	[84632-59-7]	561170	Diketopyrrolopyrrole (DPP)	base-catalyzed condensation of diisopropyl succinate with *p*-*tert*-butylbenzonitrile, followed by acidification
Pigment Red 2	[6041-94-7]	12310	Naphthol AS (Naphthol Red)	coupling diazotized 2,5-dichloroaniline with 2-hydroxy-3-naphthanilide
Pigment Red 3	[2425-85-6]	12120	Beta-Naphthol (Toluidine Red)	coupling diazotized 2-nitro-4-methylaniline with 2-naphthol
Pigment Red 5	[6410-41-9]	12490	Naphthol AS (Carmine)	coupling diazotized *N*,*N*-diethyl-4-methoxymetanilamide with 3-hydroxy-2-naphth-2’,4’-dimethoxy-5’-chloroanilide
Pigment Red 17	[6655-84-1]	12390	Naphthol AS	coupling diazotized 2-methyl-5-nitroaniline with 3-hydroxy-2-naphth-2^1-methylanilide
Pigment Red 23	[6471-49-4]	12355	Naphthol AS	coupling diazotized 2-methoxy-5-nitroaniline with 3-hydroxy-2-naphth-3^1-nitroanilide
Pigment Red 38	[6358-87-8]	21120	disazo pyrazolone (Pyrazolone Red)	coupling tetrazotized 3,3′-dichlorobenzidine with 1-phenyl-3-carbethoxy-5-pyrazolone
Pigment Red 48	[7585-41-3]	15865:1	BONA (Ba salt)	coupling diazotized 2-amino-4-chloro-
barium, calcium,	[7023-61-2]	15865:2	BONA (Ca salt)	5-methylbenzenesulfonic acid with
strontium, and	[15782-05-5]	15865:3	BONA (Sr salt)	3-hydroxy-2-naphthoic acid, followed
manganese salts	[5280-66-0]	15865:4	BONA (Mn salt) (Permanent Red 2Bs)	by salt formation
Pigment Red 49	[1103-38-4]	15630:1	Beta Naphthol (Ba salt)	coupling diazotized 2-aminonaphthalene-

Table 1 (*Continued*)

Color index (CI) name	CAS Registry Number	CI constitution number	Pigment class (common name)	Method of preparation
barium and calcium salts	[1103-39-5]	15630:2	Beta Naphthol (Ca salt)	1-sulfonic acid with 2-naphthol followed by salt formation
Pigment Red 52 calcium salt	[17852-99-2]	15860:1	BONA (Ca salt)	coupling diazotized 2-amino-4-methyl-5-chlorobenzenesulfonic acid with 3-hydroxy-2-naphthoic acid, followed by salt formation.
Pigment Red 53 barium salt	[5160-02-1]	15585:1	BONA (Ba salt) (Lake Red C)	coupling diazotized 2-amino-4-methyl- 5-chlorobenzenesulfonic acid with 2-naphthol, followed by salt formation.
Pigment Red 57 calcium salt	[5281-04-9]	15850:1	BONA (Ca salt) (Lithol Rubine B or 4B toner)	coupling diazotized 2-amino-5-methylbenzenesulfonic acid with 3-hydroxy-2-naphthoic acid, followed by salt formation.
Pigment Red 81	[12224-98-5]	45160:1	triarylcarbonium PTMA salt	salt formation between Rhodamine 6G and phosphotungstomolybdic acid (PTMA).
Pigment Red 112	[6535-46-2]	12370	Naphthol AS	coupling diazotized 2,4,5-trichloroaniline with 3-hydroxy-2-naphth-2'-methylanilide.
Pigment Red 122	[980-26-7]	73915	Quinacridone	acid-catalyzed condensation of dialkyl succinoylsuccinate with *p*-toluidine, followed by oxidation and hydrolysis, and acid-catalyzed cyclization of 2,5-di(p-toluidino)-terephthalic acid.
Pigment Red 144	[5280-78-4]	20735	disazo condensation	coupling diazotized 2,5-dichloroaniline with 3-hydroxy-2-naphthoic acid followed by acid chloride formation and reaction with 2-chloro-*p*-phenylenediamine.
Pigment Red 170	[2786-76-7]	12475	Naphthol AS	coupling diazotized *p*-aminobenzamide with 3-hydroxy-2-naphth-2^1-ethoxyanilide.
Pigment Red 177	[4051-63-2]	65300	Anthraquinone	bimolecular debromination of 1-amino-4-bromoanthraquinone-2-sulfonic acid, followed by desulfonation.
Pigment Red 179	[5521-31-3]	71130	Perylene	alkylation of perylene 1,6,7,12-tetracarboxylic acid diimide with methyl chloride or dimethyl sulfate.

Pigment Red 202	[3089-17-6]	73907	Quinacridone	acid-catalyzed condensation of dialkyl succinoylsuccinate with *p*-chloroaniline, cyclization of resulting diester to 2,9-dichloro-6,13-dihydroquinacridone, followed by oxidation.
Pigment Red 254	[122390-98-1]	56110	Diketopyrrolopyrrole (DPP)	base-catalyzed condensation of diisopropyl succinate with *p*-chlorobenzonitrile, followed by acidification.
Pigment Red 264	[88949-33-1]	561300	Diketopyrrolopyrrole (DPP)	base-catalyzed condensation of diisopropyl succinate with 4-cyanobiphenyl, followed by acidification
Pigment Violet 1	[1326-03-0]	45170:2	triarylcarbonium PTMA salt	salt formation between Rhodamine B and phosphotungstomolybdic acid.
Pigment Violet 3	[1325-82-2]	42535:2	triarylcarbonium PTMA salt	salt formation between Methyl Violet and phosphotungstomolybdic acid.
Pigment Violet 19	[1047-16-1]	73900	Quinacridone	acid-catalyzed condensation of dialkyl succinoylsuccinate with aniline, cyclization of resulting diester to 6,13-dihydroquinacridone, followed by oxidation.
Pigment Violet 23	[6358-30-1]	51319	Dioxazine (Carbazole Violet)	condensation of 3-amino-*N*-ethylcarbazole with chloranil, followed by acid-catalyzed, thermal cyclization of the diarylamino-dichlorobenzoquinone.
Pigment Blue 15	[147-14-8]	74160	Copper phthalocyanine	condensation of phthalic anhydride with urea, in presence of copper ions, with or without added chlorophthalic anhydride; subsequent conversion to alpha phase and stabilization, if necessary.
Pigment Blue 60	[81-77-6]	69800	Indanthrone	intermolecular condensation of 2-aminoanthraquinone in presence of a strong inorganic base and oxidizing agent.
Pigment Blue 1	[1325-87-7]	42595:2	triarylcarbonium PTMA salt (Victoria Blue B)	condensation of 4,4′-bis-*N*,*N*-dimethylaminobenzophenone with *N*-ethyl-1-naphtylamine, followed by oxidation and salt formation.
Pigment Blue 24	[6548-12-5]	42090:1	triarylcarbonium Ba salt (Peacock Blue)	condensation of benzaldehyde-*o*-sulfonic acid with *N*-ethyl-*N*-benzylaniline, followed by sulfonation, oxidation and salt formation.
Pigment Green 4	[61725-50-6]	42000:2	triarylcarbonium PTMA salt (Malachite Green)	condensation of benzaldehyde with *N*,*N*-dimethylaniline, followed by oxidation and salt formation.

Table 1 (*Continued*)

Color index (CI) name	CAS Registry Number	CI constitution number	Pigment class (common name)	Method of preparation
Pigment Green 7	[1328-53-6]	74260	polychloro copper phthalocyanine	chlorination of copper phthalocyanine
Pigment Green 36	[14302-13-7]	74265	polybromochloro copper phthalocyanine	bromination/chlorination of copper phthalocyanine

Table 2. **Colors of Absorbed Light and the Corresponding Complementary Colors as a Function of Wavelength**

Wavelength, nm	Color of absorbed light	Complementary color
400–420	violet	yellow-green
420–450	indigo blue	yellow
450–490	blue	orange
490–510	blue-green	red
510–530	green	purple
530–545	yellow-green	violet
545–580	yellow	indigo blue
580–630	orange	blue
630–720	red	blue-green

Table 3. **Selected Monoazo Pigments**

Pigment Yellow	CAS Registry Number	Substituents on diazonium component	Substituents on coupling component
1	[2512-29-0]	$R = NO_2$, $R_1 = CH_3$	$R_2 = R_3 = H$
2	[6486-26-6]	$R = NO_2$, $R_1 = Cl$	$R_2 = R_3 = CH_3$
3	[6486-23-3]	$R = NO_2$, $R_1 = Cl$	$R_2 = Cl$, $R_3 = H$
5	[4106-67-6]	$R = NO_2$, $R_1 = H$	$R_2 = H$, $R_3 = H$
65	[6528-34-3]	$R = NO_2$, $R_1 = OCH_3$	$R_2 = OCH_3$, $R_3 = H$
74	[6358-31-2]	$R = OCH_3$, $R_1 = NO_2$	$R_2 = OCH_3$, $R_3 = H$
75	[52320-66-8]	$R = NO_2$, $R_1 = Cl$	$R_2 = H$, $R_3 = OC_2H_5$

Table 4. **Selected Diarylide Pigments**

Pigment	CAS Registry Number	Substituents on diazonium component	Substituent on coupling component
Yellow 12	[6358-85-6]	$R = Cl$	$R_1 = R_2 = R_3 = H$
Yellow 13	[5102-83-0]	$R = Cl$	$R_1 = R_2 = CH_3$, $R_3 = H$
Yellow 14	[5468-75-7]	$R = Cl$	$R_1 = CH_3$, $R_2 = R_3 = H$
Yellow 17	[4531-49-1]	$R = Cl$	$R_1 = OCH_3$, $R_2 = R_3 = H$
Yellow 83	[5567-15-7]	$R = Cl$	$R_1 = R_3 = OCH_3$, $R_2 = Cl$
Orange 16	[6505-28-8]	$R = OCH_3$	$R_1 = R_2 = R_3 = H$

Table 5. **Typical Basic Dyes Used as Complexes with Heteropolyacids**

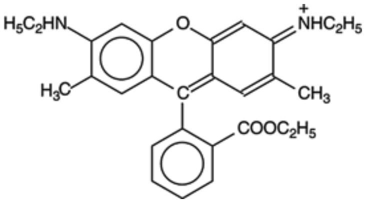
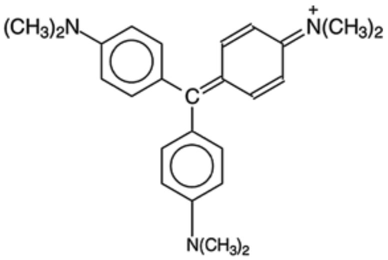
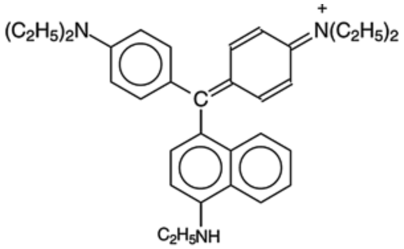
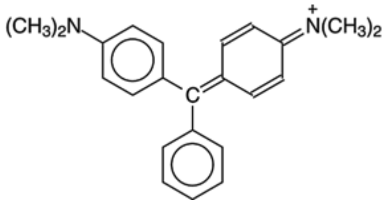
Name of dye	Structure of dye	Anion
Rhodamine (Pigment Red 81:1) CI 45160:1		PTMA
Methyl Violet (Pigment Violet 3) CI 42535:2		PTMA PMA
Victoria Blue B (Pigment Blue 1) CI 42595:2		PTMA PMA
Malachite Green (Pigment Green 4) CI 42000:2		PTMA PMA

Table 6. **Representative Commercial Quinacridone Pigments**

Pigment composition	CI designation	CAS Registry Number	Color	Structure[a]
quinacridone (QA)	PV 19	[1047-16-1]	opaque yellow-shaded red (gamma)[b]; opaque yellow-shade violet (beta)[c]	R = H
2,9-dimethyl-QA	PR 122	[980-26-7]	magenta	R = 2,9-$(CH_3)_2$
2,9-dichloro-QA	PR 202	[3089-17-6]	magenta	R = 2,9-Cl_2
quinacridone plus 4,11-di-chloroQA	PR 207	[71819-77-7]	scarlet solid solution	R = H + R = 4,11-Cl_2
quinacridone plus quinacri-donquinone	PR 206	[1503-48-6]	maroon solid solution	R = H + QAQ(R = H)

[a] See Fig. 3; especially (II) for position numbers.

[b] Also semitransparent blue-shade red (gamma).

[c] Also semitransparent and transparent violet (beta).

Table 7. **Commercial Diaryl Pyrrolopyrrole (DPP) Pigments**

Pigment identity	CI designation	CAS Registry Number	Color	Structure
diphenylDPP	PR 255	[120500-90-5]	scarlet	$R^1 = H$
di(*p*-chlorophenyl)DPP	PR 254	[122390-98-1]	red	$R^1 = Cl$
di(biphenyl)DPP	PR 264	[88949-33-1]	rubine (blue-shade red)	$R^1 = C_6H_5$
di(*p*-*tert*-butylphenyl)DPP	PO 73	[84632-59-7]	orange	$R^1 = C(CH_3)_3$

Table 8. **Commercial Perylene Pigments**

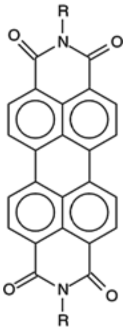
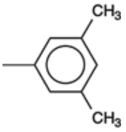
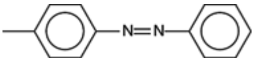
Structural formula	R	CI designation	CAS Registry Number	Color
	CH_3	PR 179	[5521-31-3]	red to maroon
		PR 149	[4948-15-6]	red
		PR 178	[3049-71-6]	red
	H	PV 29	[81-33-4]	bordeaux

Table 9. **Global Demand of Organic Pigments by Region or Country (10^6 $)**[a]

	1994	1999	2004[b]	2009[b]
North America	1128	1504	2010	2660
Latin America	93	125	185	280
Western Europe	839	1138	1525	2000
Eastern Europe	110	97	135	190
Africa/Mideast	62	94	140	205
Asia/Pacific:	724	1066	1505	2115
China	110	215	355	560
Japan	330	425	510	620
other	284	426	640	935
total:	*2956*	*4024*	*5500*	*7450*
average $/kg.	17.70	19.07	20.60	22.11
demand in 10^3 metric tons	167	211	267	337

[a] Ref. 3.

[b] Ref. 3, Freedonia Group forecasts.

Table 10. **Global Production of Organic Pigments by Pigment Type**[a]

Pigment class	Volume in 10^3 metric tons	% of total
Copper Phthalocyanines	72.2	29
Red Lakes[b]	54.8	22
Monoazo pigments	32.4	13
Disazo pigments	29.9	12
Naphthol AS pigments	19.9	8
other Azo pigments	19.9	8
Polycyclic pigments	19.9	8

[a] Ref. 4.

[b] Incldes nonazo lakes.

Table 11. **U.S. Organic Pigment and Dye Demand (10^6 $)**[a]

	1995	2000	2005[b]	2010[b]
organic pigments	995	1340	1755	2290
dyes	1585	1320	1305	1345

[a] Ref. 23.

[b] Ref. 23, Freedonia Group forecasts.

Table 12. **U.S. Exports of Organic Pigments and Preparations, by Principle Markets. Comparison of Years 1992[a] and 2002[b]**

Major	1992		2002	
markets	Quantity, t	Value, 10^3 $	Quantity, t	Value, 10^3 $
Belgium	4,160	36,684	11,353	49,435
Brazil	340	4,193	501	5,649
Canada	4,605	38,279	10,000	65,008
West Germany	927	7,477	3,951	29,253
Hong Kong	638	5,838	204	3,979
Italy	149	2,052	57	1,922
Japan	608	9,914	1,034	12,583
Mexico	866	9,196	3,250	25,462
Netherlands	252	4,130	332	4,972
Switzerland	402	8,846	1,454	22,353
U.K.	4,999	17,591	2,523	12,106
other	3,846	34,300	6,196	50,882
total	*21,793*	*178,500*	*40,855*	*283,604*

[a] Ref. 24.

[b] Ref. 25.

Table 13. **U.S. Imports of Organic Pigments and Preparations, by Specific Pigment Type, for the Year 2002**[a]

Pigment type	Quantity, t	Value, 10^3 $
P.B. 15[b]	11,834	32,740
P.B. 15	823	3,740
P.B. 15:1	1,016	10,457
P.B. 15:2	332	3,871
P.B. 15:3	2,146	12,560
P.B. 15:4	756	6,052
P.B. 16	94	3,082
P.B. 61	3	16
P.Bl 1	2,102	40,975
P.G. 7	2,343	14,239
P.G. 36	133	2,631
P.O. 31	62	206
P.O. 36	178	5,309
P.R. 57:1	1,227	5,712
P.R. 122	5	125
P.R. 144	214	3,962
P.R. 149	87	4,957
P.R. 166	22	427
P.R. 177	23	1,126
P.R. 178[c]	205	8,078
P.R. 179	75	4,314
P.R. 214	30	610
P.R. 242[d]	321	7,427
P.V. 19	154	5,094
P.V. 23	502	10,874
P.Y. 12	741	4,225
P.Y. 13	178	1,793
P.Y. 74	473	4,222
P.Y. 75	143	1,047
miscellaneous	3,784	33,028
other[e]	7,065	81,238
total:	*37,071*	*314,137*

[a] Ref. 26.

[b] Crude.

[c] Includes P.R. 101 and P.R. 138.

[d] Includes P.R. 245; P.Y. 183 and P.Y. 155.

[e] Unclassified organic pigments and preparations.

Table 14. **Global Consumption of Pigments by Industrial Sector**[a]

Industrial sector	Weight %
printing inks	53
paints and coatings	23
plastics	12
textile printing	4
fibers	3
other	5

[a] Ref. 36.

Table 15. **Worldwide Consumption of Pigments in Paints and Coatings**[a]

Industrial sector	Weight %
automotive	40
other OEM[b]	35
architectural	20
other	5

[a] Ref. 36.

[b] Original Equipment Manufacturers.

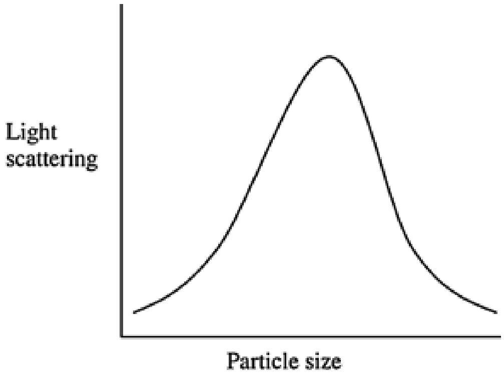


Fig. 1. The effect of particle size on light scattering.

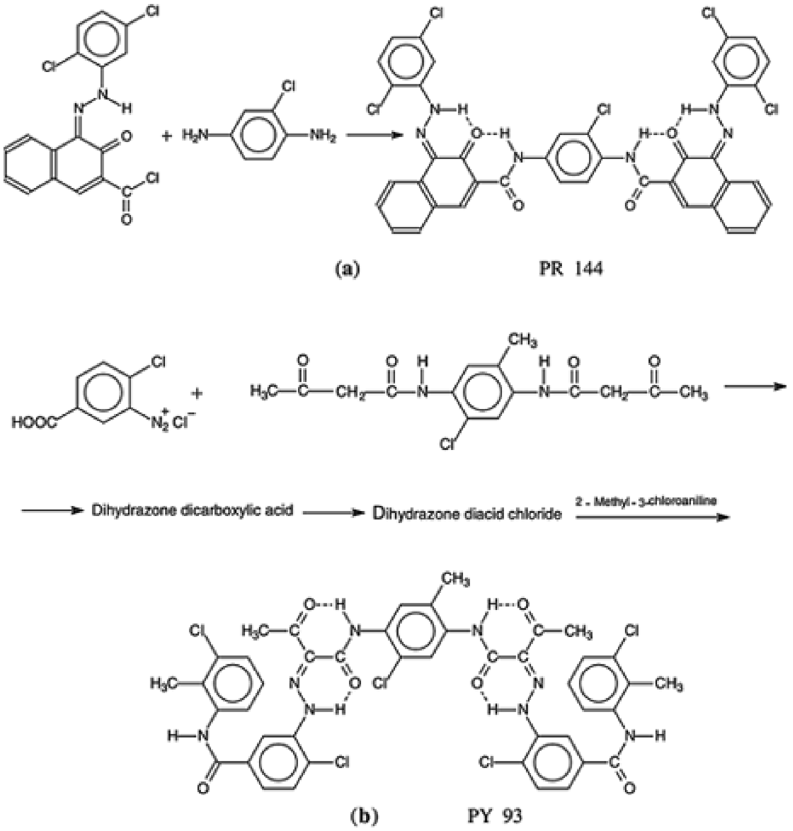


Fig. 2. Azo condensation pigments: (**a**) Pigment Red 144 and (**b**) Pigment Yellow 93.

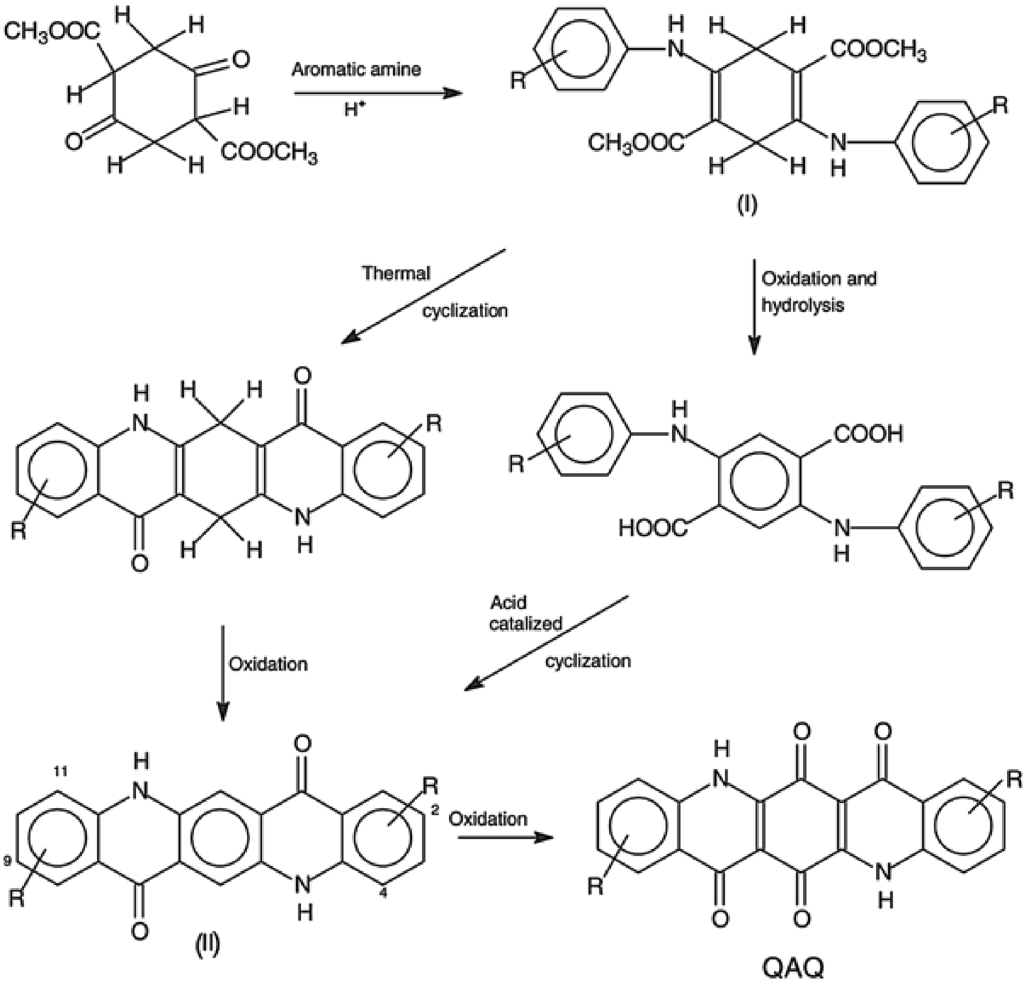


Fig. 3. Synthesis of quinacridones (II) and quinacidonequinones (QAQs).